

Amendments To The Specification

Please replace the paragraph on page 5, lines 12-13 with the following amended paragraph.

FIG. 8 7C shows a fluidized bed reactor and lock hoppers of the second embodiment according to the present invention.

Please replace the paragraph on page 8, lines 16-18 with the following amended paragraph.

High pressure hydrogen is conveyed through lines 138 to the feeders 104A, at a pressure of between 625 psi and 700 psi, preferably about 635 psi, to assist in injecting, feeding and dispersing the tar sand into reactor 104. Unless otherwise indicated the unit "psi" is pounds per square inch gage pressure. Another portion of the hydrogen gas feed from line 137 for fluidizing medium (hydrogen feed) is diverted through lines 139 and injected into the separator section 104B, at the bottom end of the reactor.

Please replace the paragraph on page 9, lines 5-10 with the following amended paragraph.

Advantageously all the high pressure hydrogen for the process of the present invention, for reaction in reactor 104 and the various heat exchange operations, is provided by the steam powered compressor 132. Compressor 132 receives fresh make-up hydrogen which is conveyed through line 130 and recycle hydrogen which is conveyed through lines 129, 140, 142, 144 and 131. Compressor 132 is powered by steam conveyed through line 162 from direct fired heater

135. 184 is the fired heater stack gases line.

Please replace the paragraph on page 9, line 23 thru page 10, line 2 with the following amended paragraph.

The hot spent tar sand is continuously discharged at a pressure of about 635 psi and a temperature of about 800°F through lock hopper valving arrangement 104B in the lower end of reactor 104 into line 105 which conveys the discharged material to spent sand heat exchangers 106 and 108. Spent sand is discharged through line 109.

Please replace the paragraph on page 10, lines 13-21 with the following amended paragraph.

The cleaned stream from the precipitator 113, product, vaporous components, and off gas, are conveyed to in-and-out heat exchanger 115 through line 114. In the in-and-out exchanger 115 the cleaned stream from line 114 is brought into indirect heat exchange relationship with hydrogen being conveyed through line 133, from compressor 132, i.e., recycle and fresh make-up hydrogen, whereby heat is transferred from the cleaned stream to the hydrogen in line 133 prior to the hydrogen stream entering the fired heater 104. The cooled and cleaned stream, products, vaporous components, off-gases, from heat exchanger 115 is discharged into line 116 while hydrogen is discharged into line 134 which conveys the hydrogen to the direct fired heater 134

135.

Please replace the paragraphs on page 11, lines 1-17 with the following amended paragraphs.

Since the gas stream has been cooled down to about 100°F and is still at a pressure of 480 psi, all carbon compounds C₃ and above have been condensed are removed from the separator 119 through flow line 155 to storage. Sour water from the separator is discharged through flow line 154. The crude oil product stream in line 155 is a mixture of naphtha and gas oils having an A.P.I. of approximately 33.5 and is a light sweet crude. The gas stream in line 120 is conveyed to a scrubbing system, e.g., at least one amine absorption column 121 where sulfur components, e.g., hydrogen sulfide and sulfur dioxide gases, are absorbed and discharged through line 122 and conveyed to a suitable sulfur recovery plant. The amine absorption system having amine absorber 121 is described in greater detail in FIG. 5.

The only gases not absorbed and removed in the absorption system having amine absorber 121 are unreacted recycle hydrogen and C₁ + C₂ hydrocarbons which are conveyed through line 129 to heat exchangers 106 so that the spent tar sand is cooled and the recycle hydrogen and C₁ + C₂ hydrocarbons is heated and discharged into line 140. The C₁ and C₂ hydrocarbons in line 129 will not be absorbed nor condensed but will be recycled with the unreacted hydrogen after processing in units 141, 143 and 145 discussed hereinafter. The C₁ and C₂ hydrocarbons will reach equilibrium within the reactor 104 at about 2% and will then add to

the production of crude oil per ton of tar sand. A small offset will be the increase in the recycle stream.

Please replace the paragraph on page 12, lines 1-3 with the following amended paragraph.

The heated and partial recycle hydrogen stream conveyed through line 140 is introduced into cyclone 141, discharged into line 142 which conveys the stream to precipitator 143, and then through line 144 for introduction into exchanger reboiler 145.

Please replace the paragraphs on page 12, line 25 thru page 15, line 21 with the following amended paragraphs.

DIRECT FIRED HEATER

As discussed above with reference to FIG. 1, a portion of the fresh make-up and cleaned recycle hydrogen from the compressor is conveyed to a direct fired heater. FIG. 3 schematically shows a fired heater 335-(135) that is designed to balance out the total energy required to operate the reactor system. Preheated air conveyed through feed lines 383-(183) is combusted with fuel in the radiant section of fired heater 335-(135) and elevates the temperature of the recycle and make-up hydrogen that is conveyed through line 334-(134). The fuel that is combusted is obtained from the C₃ fraction, e.g. propane, or natural gas produced or purchased from the described process or other sources. The hydrogen stream in lines 334-(134) has been preheated in the reactor in-out exchanger 115 to approximately 750°F. Since the hydrogen stream is

circulated through the radiant section of the heater ~~335~~ 135 the temperature of the hydrogen stream is elevated to a temperature of about 1200°F. Circulation of the hydrogen stream through line 133, 134, exchanger 115 and fired heater ~~335~~ 135 is maintained by compressor 132 so that the 1200°F hydrogen stream can be introduced via line 136 into reactor 104 (FIG. 1) or 204 (FIG. 2).

Waste heat from the radiant section of direct fired heater ~~335~~ 135 is recovered in convection section ~~335A~~-(135A), ~~335B~~-(135B) and ~~335C~~-(135C). Steam separated in drum 360 (160) is discharged into line 361-(161) and introduced into convection section ~~335A~~-(135A) where the steam temperature is raised from about 596°F to about 800°F. After passing through convection section ~~335A~~-(135A), the super heated, high pressure steam is conveyed through line 362-(162) to drive the steam turbine 163 (Fig. 4). Reduced temperature and pressure steam from turbine 163 is conveyed to steam condenser 165 and the condensate recirculated via line 166 and pump 166A (Fig. 1). The flow from pump 166A is conveyed through line 168 (368) and combined with make-up water from line 167. The water being conveyed in line ~~268~~ 168 is introduced into convection section ~~335C~~-(135C), heated and discharged through line ~~369~~-(169) for further processing, e.g., deaeration.

Steam drum 360-(160) separates steam which is conveyed to radiant section ~~335A~~-(135A) through line 161 to produce superheated steam for the turbine compressor 163.

The steam circulation loop ~~include~~ includes steam drum 360-(160), line 370-(170), recirculation pump 371-(171) and lines 372-373-(172-173) which ~~conveys~~ convey boiler water

through radiant section 335B-(135B) and back into drum 360-(160). Water for the boiler system is provided through feed line 467-(167) which flows into line 468. ~~Line 468 is similar to flow line 168, 368-168 which is in communication with line 169 through connection convection section 335a (135A) 135C to deaeration discharge.~~

As discussed above, convection section 335A-(135A) super heats steam which is conveyed through line 362-(162) to drive compressor turbine 163, which drives compressor 132. Steam is generated in convection section 335B-(135B) and make-up water and turbine condensate for boiler feed water are preheated in convection section 335C-(135C).

COMPRESSOR SYSTEM

FIG. 4, schematically shows a compressor 432-(132) driven by a high pressure steam turbine 463-(163) required to maintain circulation of gases to operate the reactor system 104. Make-up hydrogen 430-(130) and recycle hydrogen 431-(131), at approximately 450 psig and 100°F are pressurized by the compressor 432-(132) to approximately 670 psig and 122°F and discharged into line 133 which conveys and introduces the high pressure hydrogen into the in-out exchanger 115 to be further heated by exchange with reactor product gases.

High pressure steam in line 162, 362, at 1500 psig and 800°F drives the turbine 463-(163). Exhaust steam 464-(164) is condensed in condenser 465-(165), and along with make-up water 467-(167) is fed to the fired heater convection section 135C, 335C for preheating and reuse as boiler feed water make-up.

PRODUCT SEPARATION

The product separation of FIG. 1, components will be described in greater detail with reference to FIG. 5, which schematically shows the product separation from the circulating gas stream and removal of acid gasses in an amine system. Partially cooled reactor effluent gases ~~516~~(116) from the in-out exchanger 115 are further cooled in product condenser ~~517~~(117) and conveyed through line ~~518~~(118) to separator ~~519~~(119) where condensed liquids are removed as product raw crude ~~555~~(155). Overhead gases are conveyed through line ~~520~~(120) to an amine absorber ~~5A~~(121) 121 where acid gasses H₂S, CO₂ and SO₂ are absorbed by a counter current circulating amine solution. The recycle gases 121B flow from the top of the absorber ~~5A~~ 121 to recycle hydrogen stream 129.

The rich amine solution ~~5C~~ 121C exits the bottom of the absorber, flows through an amine exchanger ~~5D~~ 121D where it is heated by exchange with hot stream amine solution ~~5L~~ 121L and enters the top of an amine stripper ~~5F~~ 121F through line 121E. The lean amine solution passes through exchanger 121D to exchanger 121N via line 121M and enters 121 via lean amine feed line 121P. Absorbed acid gases are stripped from the amine solution by the application of heat to the solution in reboiler ~~545~~(145) (having reboiler feed line 146 and reboiler return line 147) and are conveyed through flow line ~~522~~(122) from the stripper to sulfur recovery off-site. Hot recycle gases are conveyed through line ~~544~~(144) from the spent sand cooler ~~145~~ 106 via cyclone 141 and precipitator 143 to provide heat for reboiler ~~545~~(145) and

the partially cooled recycled gases 5G 121G are further cooled by cooler 5H 121H and then flow through line 531-(131) to the suction side of compressor 132. Solids removed by cyclone 141 and precipitator 143 are discharged via lines 152 and 153 respectively.

Lean amine solution 5J 121J is circulated by amine circulation pumps 5K 121K through the amine exchanger 5D 121D and amine cooler 5N 121N to the top of the amine absorber 5A 121 to repeat the gas cleanup process.

Please replace the paragraphs on page 23, line 21 thru page 25, line 24 with the following amended paragraphs.

EXAMPLE 2

FIG. 7 shows another embodiment of the present invention. In this embodiment, a tar sand feed is converted into a synthetic crude oil. Run of mine tar sand from trucks is dumped into receiving, screening, and sizing equipment 702 via tar sand feed 701 for classifying tar sand at ambient temperature. The tar sand comprises bitumen and sand. The tar sand is crushed into relatively large fluidizable pieces that are capable of passing through a one inch mesh, or that are about one inch or less in size. In this embodiment, crushing the tar sand into fines or pieces less than sand size is preferably avoided to facilitate fines removal from the product stream. Limiting the amount of crushing can also reduce heat generation that can adversely affect tar sand processing. Limiting crushing can also help to preserve a water film that surrounds tar sand pieces. Tar sand pieces typically comprise an agglomeration of sand particles, each sand particle

surrounded by a film of water and an outer layer of bitumen. On contacting a hot fluidizing flow of hydrogen during later reaction steps, the water film can rapidly evaporate assisting the tar sand pieces to disintegrate into a finely fluidized dispersion of sand particles and bitumen in hydrogen.

The crushed tar sand is conveyed through conduit 703 to feed lock hoppers 704 as the feed for fluidized bed reactor 705. The feed flow through conduit 703 and between feed lock hoppers 704 is controlled by pressure feeder rotary valves ("rotary valves") 703A. 704 are lock hoppers and 703A are lock hopper valves. The bitumen in the tar sand can contain heavy metals, such as nickel, which may catalytically promote endothermic and exothermic reactions in reactor 705. However, supplemental catalyst such as, for example, nickel, cobalt, molybdenum, and vanadium can be added through catalyst feed conduit 704A the catalyst injection line to one of the feed lock hoppers 704 to assist catalysis provided by the heavy metals in the mined tar sand or shale. 704B is the reactor feed line. The reactor 705 and related equipment are shown in more detail in FIG. 8-7C.

Recycle hydrogen in conduit 725 and fresh make-up hydrogen in conduit 725A are conveyed to compressor 732. A first mixture of recycle hydrogen and makeup hydrogen exits compressor 732 in line 733, is cooled by heat exchanger 754 via feed line 733A, and passes through line 757 to feed lock hoppers 704. This cooled first hydrogen mixture helps to prevent the tar sand from gumming by keeping the tar sand cool and forces the crushed tar sand into the reactor 705 which operates at a pressure of about 600 psi. Preferably, the first hydrogen mixture reaches the lock hoppers 704 at a temperature of about 100°F or less, and maintains the tar sand

at a temperature of about 100°F or less. The tar sand is fed from feed lock hoppers 704 through conduit 704B and into reactor 705 through a feed inlet 705H the feed inlet nozzle, assisted by the first hydrogen mixture at 670 psi pressure in line 757. There are three feed lock hoppers in this embodiment, but the number may vary in other embodiments. The tar sand can be fed into the reactor approximately horizontally, near the bottom of the reactor, and just above ceramic support grid 705C. Equipment for treating mined tar sand or shale feed material and for feeding the material into the reactor, such as the equipment described above, can be referred to as a feed introducing system. Equipment for feeding tar sand or shale feed material into the reactor, such as the feed lock hoppers 704, conduit 703 and rotary valves 703A, can be referred to as a feeder device.

On entering the reactor 705 (detail in Fig. 7C), the tar sand is contacted and heated by a second hydrogen mixture. The second hydrogen mixture flows from fired heater 735 and into a gas inlet 705I the fluidizing medium inlet nozzle at the bottom of the reactor 705B through ceramic lined conduit line 736 at a temperature of about 1500°F and about 635 psi pressure. The second hydrogen mixture passes through a slotted fire brick or ceramic grid 705C before contacting the entering tar sand. The flow rate and velocity of the second hydrogen mixture are sufficient to fluidize the tar sand and to heat the tar sand to a desired reaction temperature. The heated tar sand and the second hydrogen mixture react in the reactor 705 in a fluidized bed 705E at the desired reaction temperature of about 900°F to about 1000°F, and at a pressure of about 600 psi. The second hydrogen mixture flow rate typically exceeds the minimum needed for

complete tar sand reaction with hydrogen by a factor of about 15 to about 26, and preferably by a factor of about 21. Adjustment of the second hydrogen mixture flow rate may require adjustment of other reaction parameters to maintain the fluidized bed 705E at desired pressures and temperatures. The tar sand reacts with the hydrogen mixture in the fluidized bed 705E by endothermic hydrocracking and exothermic hydrogenating reactions. Reaction products include substantially sulfur-free hydrocarbons that are condensable into hydrocarbon liquids at standard temperature and pressure.

Reaction products including synthetic crude oil and unreacted hydrogen mixture exit the reactor 705 through a product stream outlet 705F the reactor outlet nozzle as an overhead or product stream through cyclone separators 705A and into exit conduit line 710. Solids entrained in the overhead product stream, such as sand particles and fines, are trapped by the cyclone separators 705A and are deposited near the ceramic screen 705C ~~at the bottom of the reactor over reactor bottom~~ 705B, where they are again entrained in the fluidized bed 705E. Eventually, the spent sand and solids exit the reactor 705 through a conduit line 705D the spent sand outlet line. The overhead stream flows through a hydrogen recycling system wherein hydrogen is removed from the remainder of the overhead stream, treated, and returned to the reactor.

Please replace the paragraph on page 26, lines 12-17 with the following amended paragraph.

Spent sand, at a temperature of about 950°F, overflows from reactor 705 into conduit line 705D through a spent solids outlet 705G the spent sand outlet nozzle. The height of the conduit line 705D may establish the maximum height of the fluidized bed 705E. The sand then flows through spent sand lock hoppers 706, through conduit line 707 and into rotary coolers 708 which cool the sand from a temperature of 950°F to about 665°F. Spent sand is discharged through line 709. The cooled sand can be discharged and used, for example, for land reclamation.

Please replace the paragraph on page 27, line 4 thru page 28, line 9 with the following amended paragraph.

The reactor overhead stream from the cyclone separator 705A is discharged into line 710 the reactor product gas outlet line, and then to hot gas clean-up 711. The overhead stream in line 710 exits the reactor 705 at about 950°F and enters the hot gas clean-up 711. Ceramic bag collectors or filters in the hot gas clean-up 711 remove and collect fines remaining in the overhead stream. The filters are periodically pulsated by a back flow of a 650 psi, 875°F hydrogen mixture taken from in-out heat exchanger 715 via conduit line 734A. Collected fine fines and solids are removed from the bottom of the hot gas clean-up 711 and are collected in hot gas clean-up lock hoppers 712. The fines can be combined with spent sand and used for land reclamation. The disposal of the dry sand and fines resulting from this invention is environmentally preferable to existing wet disposal systems.

The substantially solids-free overhead stream flows from the hot gas clean-up through hot

gas clean-up overhead line 713 to the in-out heat exchanger 715. The in-out heat exchanger 715 is an indirect heat exchanger wherein heat is transferred from the overhead stream to a portion of the hydrogen mixture exiting compressor 732 via conduit 733. The heated hydrogen mixture is conveyed via a conduit line 734 to the fired heater 735. The cooled overhead stream exits the in-out heat exchanger 715 through line 716. 736 is the fluidizing medium inlet line to the reactor 705.

The overhead stream in line 716 enters condenser 717 where condensable vapors and gases are condensed. The overhead stream exits the condenser 717 in line 718 at a temperature of about 100°F and passes to a first separator 719 where the sour water is purged separated from the liquid product and removed overhead stream via line 786. The liquid product overhead stream, now purged of sour water, passes to a second separator 721 via conduit line 720 where a small vapor letdown stream is separated from the liquid product overhead stream and flows through line 722 to fired heater 735. 722 is the vapor letdown stream line from 721. Also, carbon compounds C₃ and above are condensed degassified and removed by from the second separator 721 and through flow through line 790 as a light substantially sulfur-free synthetic crude oil product stream comprising a mixture of naphtha and gas oils having an A.P.I. gravity of approximately 33.5. The crude oil product stream in conduit line 790 flows to storage and shipping. The overhead gas stream remaining fluid in from the separator 719 721, including recycle hydrogen, is at a temperature of about 100°F and 480 psi pressure and discharges from the separator 719 721 as a stream in via line 723 to a scrubbing system. The scrubbing system

(Fig. 7B) typically comprises at least one amine absorption column 724 where sulfur components, for example, hydrogen sulfide and sulfur dioxide gases, are absorbed and discharged through line 744 from regenerator 743. A sulfur recovery system can be used to recover sulfur from the sulfur components.

Please replace the paragraph on page 28, line 10 with the following amended paragraph.

The absorber 724 can comprise, for example, a counter current circulating ethanol amine solution in intimate contact with the remaining overhead stream. The remaining fluid overhead stream can comprise gases such as, for example, H₂S, CO₂, SO₂, NH₃, recycle hydrogen, and C₁ and C₂ hydrocarbons. H₂S, CO₂, SO₂, and NH₃ are removed from the remaining fluid overhead stream by the absorber 724. Remaining hydrogen, C₁ and C₂ hydrocarbons form the recycle hydrogen mixture and flow through line 725 to compressor 732.

Please replace the paragraphs on page 28, line 16 thru page 29, line 3 with the following amended paragraphs.

The rich amine solution having absorbed H₂S, CO₂, SO₂ and NH₃ is discharged from the absorber 724 through line 740 and flows through an amine heat exchanger 741. In the amine heat exchanger 741 the rich amine solution is heated by exchange with hot amine solution in line 750 which is returning from amine regenerator 743 to the absorber 724. The heated rich amine solution flows through line 742 and enters the top of the amine regenerator 743. Absorbed acid

gases are stripped from the rich amine solution by further heating the rich solution using steam in ~~from~~ a steam reboiler 745. Heat for the reboiler 745 is supplied by steam from the fired heater 735 steam recovery system. Reboiler 745 is fed amine solution by reboiler feed line 746 and discharges it back to regenerator 743 through reboiler return line 747.

Lean amine solution is discharged from the regenerator 743 in line 748 and is circulated by an amine circulation pump 749 through amine exchanger 741 and amine cooler 752 to the top of the amine absorber 724. The effluent of 741 is fed by line 751 to amine cooler 752 which in turn feeds Absorber 724 via line 753.

Please replace the paragraph on page 29, lines 12-16 with the following amended paragraph.

The compressor 732 pressurizes the recycle hydrogen mixture and make-up hydrogen from 450 psi to approximately 670 psi and 187 °F and ~~discharge~~ discharges the hydrogen mixture into line 733. A portion of the hydrogen mixture in line 733 is the first hydrogen mixture and is delivered to heat exchanger 754 via line 733A. Another portion of the hydrogen mixture in line 733 is the second hydrogen mixture and is delivered to the in-out heat exchanger 715.

Please replace the paragraph on page 29, lines 17-24 with the following amended paragraph.

The heat exchanger 754 cools the first hydrogen mixture from about 187°F to 100°F. A

portion of the first hydrogen mixture in line 757 flows into line 756 and to a C₁ and C₂ hydrocarbon pressure swing adsorption ("PSA") system 755. The PSA system helps to maintain the C₁ and C₂ hydrocarbon level in the first and the second hydrocarbon mixture at about 2% - 3%. C₁ and C₂ ~~hydrocarbon hydrocarbons~~ purged from the first hydrocarbon mixture ~~are~~ is discharged through line 758 and combined with the gas in line ~~22~~ 722 which is delivered to the fired heater 735. Purified hydrogen produced by the PSA 755 flows through line 756A and back to the suction of compressor 732 via line 725. 757 is the lock hopper motivation gas line.

Please replace the paragraph on page 30, lines 8-18 with the following amended paragraph.

Waste heat from the radiant section of direct fired heater 735 is recovered in convection sections 735A, 735B and 735C. Steam and water are discharged from a steam drum 760 ~~into~~ through the fired heater 735 convection section. 772 is the circulating boiler water line. Heated steam is returned to the drum via line 773. Steam separated from water in drum 760 is discharged into line 761 and introduced into convection section 735A where the steam temperature is raised from about 596°F to about 800°F. After passing through convection section 735A, the super heated, high pressure steam is conveyed through line 762 to drive the steam turbine 763. Reduced temperature and pressure steam from turbine 763 is conveyed to steam condenser 765 and the condensate recirculated via line 767. The flow from pump 766A is conveyed through line 767 and combined with make-up water. The water being conveyed in line 767 is introduced into convection section 735C, heated and discharged through line ~~736~~ 769 for

further processing, such as aeration deaeration. 769 is the preheated boiler feed water line to
deaeration. 784 is the fired heater stack gases line.